



Quantitative assessment of organosulfates in size-segregated rural fine aerosol

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**Quantification of
organosulfates in
rural aerosol**

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Quantitative assessment of organosulfates in size-segregated rural fine aerosol

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Abstract

Organosulfates have recently come into the focus of organic aerosol research as potentially important components of water-soluble secondary organic aerosol (SOA) which now dominate tropospheric fine aerosol. Their presence has been confirmed by the identification of sulfate esters of abundant biogenic carbonyl compounds in both smog chamber and continental aerosol. However, none of the studies have been able to determine the mass contribution of organosulfates to SOA.

In this paper, as possibly the very first attempt to quantify organosulfates in ambient aerosol, we inferred the mass concentrations of organosulfates by concurrently determining mass concentrations of total sulfur, sulfate and methanesulfonate in rural fine aerosol using two highly sensitive analytical techniques. Although uncertainties were relatively large, we found that mass concentrations of organosulfates in water-soluble fine aerosol ranged from $0.02 \mu\text{gS m}^{-3}$ to $0.09 \mu\text{gS m}^{-3}$ yielding a mass contribution of 6–12% to bulk sulfur concentrations (or 6–14% to sulfate concentrations). The inferred size distribution of organosulfates suggested that they possibly form in heterogeneous reactions from semi-volatile carbonyl compounds with subsequent or concurrent condensation of gaseous sulfuric acid producing a refractory organic film on particle surfaces.

1 Introduction

Organic aerosol is now a major constituent of tropospheric fine aerosol and its effects are becoming increasingly important in determining climatic and other effects of atmospheric aerosol. A significant fraction of organic aerosol is formed in the atmosphere as secondary organic aerosol (SOA) (Kroll and Seinfeld, 2008). It is generally agreed that current atmospheric models based on the traditional concepts of SOA formation severely underestimate SOA mass concentrations observed in most parts of the troposphere. Ten years ago it was already suggested that besides photooxidation of volatile

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organic compounds and subsequent gas-to-particle partitioning of semi- or less volatile oxidation products, heterogeneous and multiphase processes may play an important yet poorly understood role in SOA formation (Ravishankara, 1997). Since then, significant progress has been made on these fields, and our understanding regarding the importance of these processes in the atmosphere has been improving.

It has been shown quite recently that heterogeneous reactions involving acidic seed aerosol significantly enhance secondary organic aerosol (SOA) yields in controlled smog chamber experiments (Jang and Kamens, 2001; Jang et al., 2002). The volatile organic compounds involved in such studies were well-known aerosol precursors such as α -pinene (Czoschke et al., 2003; Gao et al., 2004a,b; Iinuma et al., 2004; Kleindienst et al., 2006; Czoschke and Jang, 2006; Jang et al., 2006), β -pinene (Iinuma et al., 2007b; Northcross and Jang, 2007), limonene (Iinuma et al., 2004; Northcross and Jang, 2007), and isoprene (Czoschke et al., 2003), or directly their semi-volatile photooxidation products like pinonaldehyde (Liggio and Li, 2006a,b), glyoxal (Kroll et al., 2005; Liggio et al., 2005), or other carbonyls (Jang et al., 2003, 2004, 2005). Similar reactions can be induced by photooxidation of aerosol precursors and SO₂ (Surratt et al., 2007). It has been shown recently that on highly acidic particles even the direct uptake of isoprene and α -pinene is possible, i.e. without any prior photooxidation step (Liggio et al., 2007), confirming the hypothesis based on previous bulk experiments (Limbeck et al., 2003).

Albeit the mechanisms behind the enhanced uptake are still largely unknown, recent mass spectrometric evidences suggest that organosulfate (sulfate esters and their derivatives) formation is involved (Surratt et al., 2007). Such compounds have been detected in limonene photooxidation experiments in which no apparent increase in SOA yield was detected with increasing seed acidity (Iinuma et al., 2007a). Matrix-assisted laser desorption ionization-MS measurements conducted on smog-chamber aerosol indicated that sulfate diester formation or sulfate ester oligomerization reactions may also be possible (Surratt et al., 2007). It was also demonstrated in smog-chamber experiments that high NO_x mixing ratios strongly suppressed organosulfate formation

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possibly because organic acid formation was favored at the expense of esterification reactions (Surratt et al., 2007).

It has also been shown that organosulfates are thermally stable even at the high temperatures of the analytical instruments and do not interfere with ion chromatographic inorganic sulfate measurements (Liggio and Li, 2006; Surratt et al., 2007), but partially revert to inorganic sulfate during detection in aerosol mass spectrometry (Liggio and Li, 2006). For isoprene, enhancement of sulfate ester signals in the presence of acidic seed aerosol was largely in the same order as in previous SOA yield observations (Surratt et al., 2007). As an additional indirect evidence, inorganic sulfate was shown to decrease in line with the emergence of organosulfate signals. Additional experiments excluded that organosulfates can be sampling or measurement artifacts (Surratt et al., 2007).

In addition to smog-chamber studies, a few field measurements indicated the presence of specific sulfate esters (also identified in follow-up smog-chamber studies) using LC-ESI-MS (Gao et al., 2006; Surratt et al., 2007; Iinuma et al., 2007), or the presence of organosulfur functional groups by FTIR (Blando et al., 1998; Gilardoni et al., 2007) implying that the chemistry occurring in smog-chamber experiments may be relevant under ambient conditions in spite of the significantly lower VOC mixing ratios, higher RH and possibly lower aerosol acidity. A recent study on water-soluble HULIS fraction of urban and rural aerosol also suggested that organosulfates are present in the high MW fraction of the organic aerosol as well (Romero and Oehme, 2005). Ultra high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry implied the presence of a large number of sulfur containing organic compounds (Reemtsma et al., 2006). Similarly, FT-ICR-MS with even higher mass resolution has been applied for rural aerosol collected under conditions conducive to photochemical smog formation and identified a large number of water-soluble organic compounds containing one sulfur atom (Schmitt-Kopplin et al., 2008¹). It is very likely that under ambient conditions volatile organic compounds other than those studied in the laboratory (including other

¹ Schmitt-Kopplin et al., in preparation, 2008.

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monoterpenes, sesquiterpenes, or aromatic compounds) are able to produce particle-phase organosulfates and thus contribute to SOA.

Among other potential sulfur compounds methanesulfonate (MSA) is by far the most abundant species which is formed in the photooxidation of dimethylsulfide (DMS) (von Glasow and Crutzen, 2004). However, this compound was reported to occur in concentrations in the order of 60–110 ng m⁻³ (corresponding to sulfur-equivalent mass concentrations of 20–37 ng S m⁻³) predominantly in the marine atmosphere (Quinn et al., 2000; Kouvarakis and Mihalopoulos, 2002; Mihalopoulos et al., 2007). Continental measurements of MSA are sparse, but a recent study conducted reported mass concentrations of MSA, if detected at all, around 10 ng S m⁻³ (Ocskay et al., 2006). This makes it very likely that organosulfates are quantitatively the most important components among water-soluble organic sulfur compounds.

Despite the emerging evidence from both smog-chamber studies and ambient aerosol measurements that organosulfates may explain a significant part of the hitherto unknown fraction of SOA, all of the studies made so far have lacked the quantitative aspect how important this class of compounds can be on a mass basis. This is because the mass spectrometric techniques used in the above studies to assign chemical structures or even exact elemental composition of specific sulfur containing compounds are not suitable to determine mass concentrations of individual compounds when standards are not available, or of organic sulfur in bulk. Without this information, however, it is very difficult to assess the contribution of organosulfates to atmospheric SOA, and to incorporate them into atmospheric models. Thus the magnitude of the effects these compounds likely play in the troposphere remains essentially unknown.

In this study we used two highly sensitive analytical techniques to determine mass concentrations of total (bulk) sulfur and both sulfate and methanesulfonate ions concurrently in aqueous extracts of size-segregated rural aerosol. The mass concentrations of organic sulfur were inferred as a difference between the results of two independent measurements. Extreme care was taken to minimize the discrepancies between the two methods, and uncertainties were carefully evaluated. To the best of our knowledge,

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our method is the first attempt to quantitatively assess the contribution of organosulfates to both SOA and sulfate aerosols.

2 Experimental

2.1 Sampling and sample preparation

5 Aerosol samples were taken in May and June 2006 at K-pusztá, Hungary. The Hungarian background air-pollution monitoring station, K-pusztá is situated on a forest clearing of the Great Hungarian Plain, 136 m a.s.l. Since the station is located in a confined area relatively far from anthropogenic sources (the only nearby town is about 15 km SE from the station while the prevailing wind direction is WNW) samples collected at K-pusztá likely represent the Central European regional air.

10 Aerosol samples were taken for 48 h with an 8-stage Berner impactor with cut-off sizes from 0.0625 to 16 μm (0.0625, 0.125, 0.25, 0.5, 1, 2, 4, 8, 16 μm). Since organosulfates are assumed to be secondary aerosol constituents and all related smog-chamber experiments were confined to the fine aerosol mode, in this work we focussed only on particles smaller than 2 μm diameter (impactor stages 1–5). The air was sampled at a height of 10 m above the surface under ambient conditions, at a flow rate of 1.878 m^3h^{-1} . The aerosol samples were collected on pre-cleaned Al-foils and stored in the freezer until analysis.

20 One quarter of each Al-foil was extracted with 2 ml Milli-Q water for 24 h. The extracts were filtered through Millex-HV Durapore membrane filters (0.22 μm pore diameter) in order to remove particles suspended in the solutions. The extracts were divided in two for further analyses.

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2.2 Analytical methods

Water soluble total sulfur ($S_{\text{total}}, \mu\text{gS m}^{-3}$), sulfate ions ($S_{\text{sulfate}}, \mu\text{gS m}^{-3}$) and methanesulfonate ($S_{\text{MSA}}, \mu\text{gS m}^{-3}$) concentrations were determined in aqueous aerosol extracts by two independent methods. In order to minimize the possible biases of sampling and sample handling, the very same extract was simultaneously analyzed by the two methods which were calibrated using the same standard solution. These precautions were necessary since the mass concentrations of organic sulfur were obtained as a difference between the two relatively large values of measured concentrations. Although the relative estimates are not affected, absolute concentrations might be loaded with an additional bias which arose from the fact that the measurements were taken from one quarter of each impactor plate.

2.2.1 Determination of S_{sulfate} and S_{MSA}

Mass concentrations of sulfate and methanesulfonate ions were analyzed by ion chromatography. The aerosol extracts were injected directly without any further preparation.

All the reagents employed were of analytical grade (Fluka Chemie AG, Buchs, Switzerland). All aqueous solutions were prepared in high purity water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$ resistivity) obtained with a Milli-Q Plus apparatus (Millipore, Bedford, MA, USA).

Ion chromatographic measurements were performed with a Dionex DX300 gradient chromatographic system (Dionex, Sunnyvale, CA, USA), which consisted of a CHA-6 high pressure chromatographic module, Dionex EDM eluent degas module, gradient pump and a conductivity detector CDM-II. Chromatograms were recorded digitally using Dionex ACI advanced computer interface and Dionex AI 450 software. Model 9125 injection unit (Rheodyne, Rohnert Park, CA, USA) was applied containing a $100 \mu\text{l}$ injection loop. Separations were carried out on a Dionex IonPac AS9-HC, $250 \times 4 \text{ mm}$, analytical column with a capacity of $190 \mu\text{eq}$. The column substrate was a $9 \mu\text{m}$ diameter macroporous (2000 \AA) resin bead, consisting of ethylvinylbenzene crosslinked with 55% divinylbenzene. The anion exchange layer was functionalized with quaternary

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ammonium groups.

This anion exchange layer had a controlled thickness. 11 mM sodium carbonate solution was used as an eluent which was stored under He atmosphere and was prepared daily. The conductivity of the eluent was suppressed with a Dionex AMMS-II suppressor continuously regenerated by 25 mM sulfuric acid with a flow rate of 3.5 ml min^{-1} . All samples were analyzed in triplicate with a flow rate of 1 ml min^{-1} .

Sensitivity of the method for sulfate ions was $138.53 \mu\text{S ppm}^{-1} \text{ S}$, Lower Limit of Detection (LLD) was 0.09 ppm S , R^2 value of the analytical curve was 0.999. RSD values varied between 1.3 and 7.8%, (average 2.3%).

Since formate and methanesulfonate co-eluted under the conditions of separation (Fig. 1) the determination of mass concentrations of methanesulfonate required the resolution of the two overlapped peaks. The resolution was carried out by fitting exponentially modified Gaussian (EMG) functions on the envelope of overlapping peak profiles. The parameters of EMG curves described the shape of the individual formate and methanesulfonate peaks were determined prior to the calculations. The determined values then were used as initial parameters during the mathematical resolution of peaks of formate and methanesulfonate (Felinger, 1998). The concentrations of methanesulfonate in the samples were calculated on the basis of the calculated area of the resolved peak of this component.

Sensitivity of the method for methanesulfonate was $1.14 \mu\text{S ppm}^{-1} \text{ S}$, the estimated Lower Limit of Detection (LLD) was 0.18 ppm S , R^2 value of the analytical curve was 0.999. RSD values varied between 0.7 and 9.6% (average 5.1%).

2.2.2 Determination of S_{total}

Mass concentrations of water soluble total sulfur (S_{total}) were determined by a sensitive X-Ray fluorescence spectrometric (XRF) method which was developed for direct analysis of the chemical composition of aerosol samples (Szilágyi et al., 2004).

A PHILIPS PW 2404 wavelength dispersive X-ray fluorescence spectrometer equipped with a 4 kW Rh anode tube (32 KV, 125 mA) was applied, flow counter was

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used as a detector, the collimator was 300 μm , while the analyzing crystal was Ge 111-C, with 2 θ ragg angle of 110.52°. Total counting time on SK α line was 40 s.

A liquid sample holder with 6 μm thick Mylar foil was placed in a steel sample holder cup with an inner diameter of 27 mm. Both standards and samples to be analyzed were applied facing the X-ray source and covered with a Re plate. Applying Re plate as a secondary target resulted in increased sensitivity of the SK α line.

250 μl of the aerosol extracts were applied on fixed sized Al-foils and dried at room temperature in a closed glass box under a gentle flow of nitrogen. Calibration was performed in triplicate with standard solutions of Na₂SO₄ in the range of 0–1.5 μgS absolute. Sensitivity of the method was 1.69 kcps μgS^{-1} , Lower Limit of Detection (LLD) was 0.01 μgS . R^2 value of the analytical curve was 0.995, RSD values varied between 2 and 11% (average 6%) except for the blank for which the RSD was 27%.

2.2.3 Estimation of uncertainties

The relative standard deviations accompanying the measurements were calculated using the statistical rules of error propagation.

The relative standard deviation of the measured intensities was estimated to be 10% based on the RSD values reported above. For the ion-chromatographic measurements an RSD value of 3% were applied, based on the measured values. The concentration of the methanesulfonate was determined in 2 set of samples. The concentration of MSA was found to be 1–3% of the sulfate concentration on each plate. Thus for the MSA concentrations we assumed that its concentration varied within 95% probability level between 1 and 3% of the sulfate concentrations. We also took account the possible error of the sample divisions (quartering the impaction foils). For quartering the sample foils we used a template. We considered this error by 3% uncertainty in the area of the analyzed foil.

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3 Results and discussion

3.1 Mass concentration of organosulfates

The concentrations of S_{total} , S_{sulfate} , S_{MSA} reported in Table 1 were calculated as a sum of the concentrations measured in each impactor stages. The relative standard deviations are calculated from the standard deviations of the measured quantities in each stage taking into account the uncertainty of foil quartering and the error propagation.

Mass concentrations of organic sulfur (S_{org} , $\mu\text{gS m}^{-3}$) were estimated as the sum of differences between the mass concentrations of total sulfur (S_{total} , $\mu\text{gS m}^{-3}$) and of sulfate (S_{sulfate} , $\mu\text{gS m}^{-3}$) and methanesulfonate (S_{MSA} , $\mu\text{gS m}^{-3}$) ions in aqueous extracts of the five impactor stages of each sample. As shown in Table 1, mass concentrations of organic sulfur in fine aerosol ranged from $0.02 \mu\text{gS m}^{-3}$ to $0.09 \mu\text{gS m}^{-3}$ representing 6–12% of bulk sulfur concentrations (or 6–14% of sulfate concentrations). In spite of the relatively high RSD values of the organosulfate concentrations, it can be clearly seen that its concentration is not negligible in the summer-time fine aerosol in K-pusztá.

In our method the mass concentration of water-soluble organic sulfur was indirectly estimated as the difference between the sulfur-equivalent mass concentrations of total sulfur and sulfate plus methanesulfonate, but there was no explicit information on the chemical character of the compounds. However, structure elucidation of sulfur-containing compounds by ESI-MS (Gao et al., 2006; Surratt et al., 2007) or FTIR spectrometry (Blando et al., 1998; Gilardoni et al., 2007), and determination of elemental compositions of a large number of organic species by ultra high-resolution ion cyclotron resonance mass spectrometry in continental aerosol (Reentsma et al., 2006; Schmitt-Kopplin et al., 2008¹) all imply that sulfate esters (organosulfates) and their derivatives may be the dominant form of organic sulfur compounds in water-soluble continental aerosol. This assumption is also supported by several smog-chamber studies which observed the formation of organosulfates during the photooxidation of various volatile

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organic compounds in the presence of acidic seed aerosols or SO₂.

3.2 Size distribution of organic sulfur

As far as the origin of organosulfates is concerned, both the magnitude of mass concentration of organosulfates and their size distribution imply a potential formation mechanism. Regarding the size distributions of total (bulk) and sulfate-methanesulfonate ions (Fig. 2) in the nucleation mode virtually no excess sulfur was found within the range of uncertainty. This finding may imply that the reactive uptake of unsaturated volatile organic compounds or their gas-phase photooxidation products on freshly formed highly acidic particles may not be a significant process on a mass basis. Both absolute and relative (to sulfate) mass concentrations of organosulfates peaked in the accumulation mode particles, in the range in which the effective surface size distribution of fine aerosol is typically at its maximum. Thus a possible heterogeneous mechanism of organosulfate formation is the partitioning of semi-volatile carbonyl compounds with subsequent or concurrent condensation of sulfuric acid formed in gas-phase photooxidation reactions, and chemical reactions on the particle surface producing a refractory organic film. There was an indication in a previous transmission electron microscopic study on accumulation mode summertime aerosol from the same site (Pósfai and Molnár, 2000) that such films do exist on typical ammonium-sulfate particles and can withstand the electron beam and high vacuum of the electron microscope. This reaction mechanism exerts no driving force for significant direct uptake of isoprene or monoterpenes, thus organosulfate formation should be preceded by gas-phase photooxidation reactions producing semi-volatile carbonyl compounds which are capable of partitioning into the aerosol phase. Esterification reactions on the surface provide a continuous sink for these semi-volatile carbonyls and thus lead to significant SOA formation compared to physical partitioning.

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4 Conclusions

In this work, as likely the very first attempt to quantify organosulfates in ambient aerosol, we inferred the mass concentrations of organic sulfur by difference from concurrently determined mass concentrations of total sulfur, sulfate and methanesulfonate in size-segregated rural fine aerosol. Based on chemical information available in the literature, we assumed that most of the organic sulfur compounds were likely organic sulfate esters (organosulfates). Admitting that the uncertainties accompanying the indirect determination were relatively large, we found that mass concentrations of organosulfates in water-soluble rural fine aerosol ranged from $0.02 \mu\text{gS m}^{-3}$ to $0.09 \mu\text{gS m}^{-3}$ yielding a mass contribution of 6–12% to bulk sulfur concentrations (or 6–14% to sulfate concentrations). Since sulfate is soluble in water but some part of organosulfates (e.g. high MW species) may not be, these values likely represent a lowerbound estimate for the organosulfate contribution. The inferred size distribution of organosulfates suggested that they possibly formed in heterogeneous reactions from semi-volatile carbonyl compounds with subsequent or concurrent condensation of gaseous sulfuric acid producing a refractory organic film on particle surfaces.

Since the number of samples was very limited and sampling was confined to a single location and time-period, the tropospheric abundance of this compound class cannot be reliably assessed. However, our results suggest, in line with conclusions drawn from specific qualitative ambient aerosol measurements as well as implicitly from smog chamber studies, that organosulfates may represent a substantial mass fraction of the hitherto unknown part of SOA in rural aerosol in summer. Furthermore, the sulfur bound in these compounds add a sizable mass to the sulfur bound as sulfate, and thus it might not be overlooked in the global sulfur budget. However in these fields further studies are clearly warranted.

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Table 1. Total mass concentrations of total (bulk) sulfur (S_{total} , $\mu\text{gS m}^{-3}$), sulfate (S_{sulfate} , $\mu\text{gS m}^{-3}$) and methanesulfonate ions (S_{MSA} , $\mu\text{gS m}^{-3}$) and organosulfates, with corresponding relative standard deviations (see discussion below for details) (S_{org} , $\mu\text{gS m}^{-3}$), and the ratio of organosulfates to total (bulk) sulfur and to sulfate ions (%) (with relative standard deviations) in aqueous extracts of fine aerosol samples collected at K-puszta (Hungary) in May and June 2006.

Sampling period	S_{total}		S_{sulfate}		S_{MSA}		S_{org}		$S_{\text{org}}/S_{\text{total}}$		$S_{\text{org}}/S_{\text{sulfate}}$	
	average ($\mu\text{gS m}^{-3}$)	RSD (%)	average ($\mu\text{gS m}^{-3}$)	RSD (%)	average ($\mu\text{gS m}^{-3}$)	RSD (%)	Average ($\mu\text{gS m}^{-3}$)	RSD (%)	average (%)	RSD (%)	average (%)	RSD (%)
29–31 May	0.57	6.7	0.50	2.4	0.010	14	0.06	63	11	64	13	63
4–6 June	0.70	6.8	0.60	2.5	0.012	14	0.09	58	12	58	14	58
6–8 June	0.70	7.0	0.63	2.5	0.013	15	0.05	96	7.7	96	8.5	96
14–16 June	0.38	7.3	0.35	2.4	0.007	14	0.02	129	5.9	129	6.4	129

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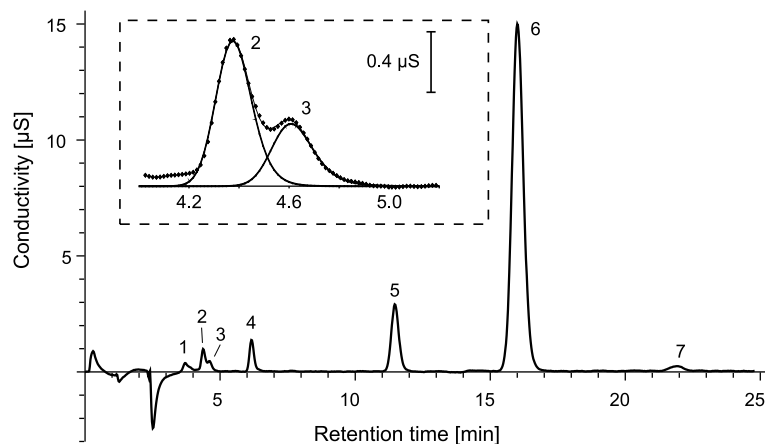


Fig. 1. Ion chromatogram of the aqueous aerosol extract (0.25–0.5 μm particle diameter) from the sample collected between 6–8 June, 2006. Peaks: 1: unknown, 2: formate, 3: methane-sulfonate, 4: chloride, 5: nitrate, 6: sulfate, and 7: oxalate. The peaks of formate and methane-sulfonate resolved by curve fitting can be seen in the dashed box.

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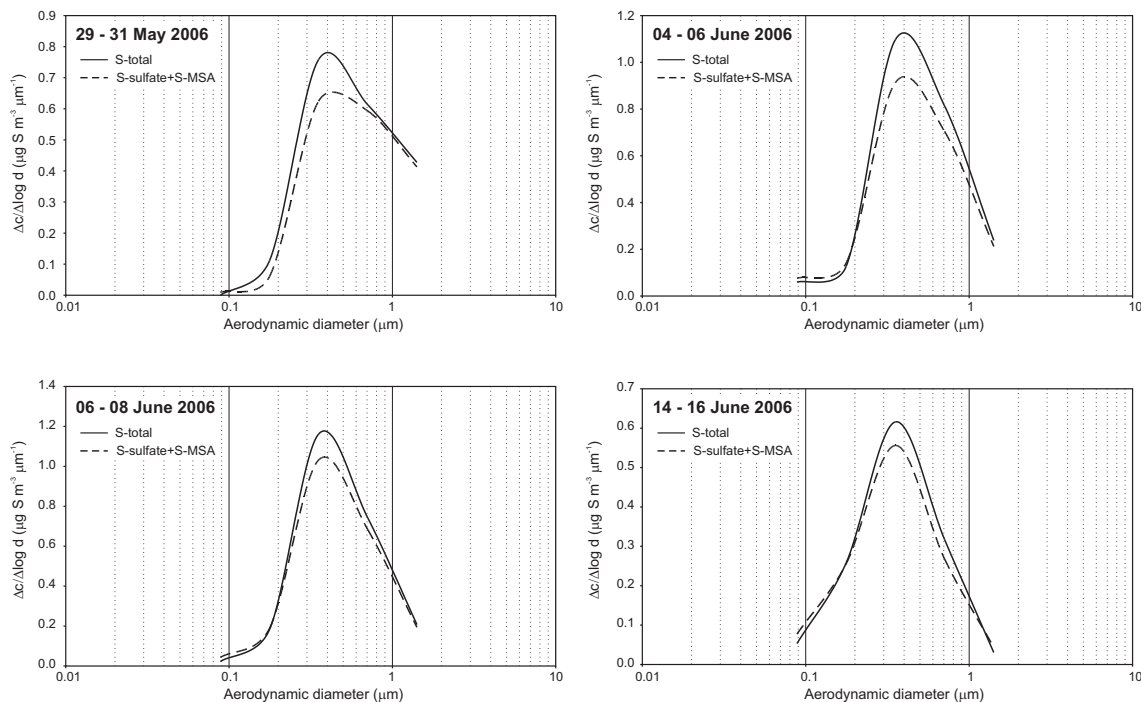


Fig. 2. Size distribution of total (bulk) sulfur, sulfate plus methanesulfonate ions (dashed line) each given in $\Delta c/\Delta \log d$ ($\mu\text{g S m}^{-3} \mu\text{m}^{-1}$), in aqueous extracts of aerosol samples collected at K-pusztá (Hungary) in May and June 2006.

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